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PLANETARY AERONOMY XI:  
ABSOLUTE INTENSITY MEASUREMENTS IN  
THE VACUUM ULTRAVIOLET

J. A. R. SAMSON

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## I. INTRODUCTION

Techniques to measure the absolute intensity of radiation in the visible and infrared region of the spectrum are well established. The technique usually involves the calibration of the response of a thermopile or some other detector to radiation emitted from a National Bureau of Standards lamp. These "secondary" standards are then used to determine the absolute intensity of the unknown radiation. Unfortunately, in the extreme ultraviolet region of the spectrum, the flux density emitted by most light sources is far weaker than in the visible, especially after transmission through a monochromator where the initial radiation intensity is greatly attenuated by the poor reflectivity of gratings.<sup>(1)</sup> Thus, it becomes more difficult to use a thermopile to achieve accurate measurements.

This report confines itself to intensity measurements in the vacuum ultraviolet region of the spectrum. This is the region where most gases ionize — certainly, all of the major atmospheric gases. A very important parameter in the study of planetary atmospheres and in upper atmospheric research is the photoionization cross section. To obtain this parameter, it is essential to know the absolute intensity of the ionizing radiation. This is the motivation for the present investigation; however, the importance of intensity measurements far exceeds that of measuring only photoionization cross sections. For example, the present generation of solar extreme ultraviolet measurements are made with either uncalibrated or

poorly calibrated detectors, mainly because of the extreme difficulties encountered in this spectral region.

## II. METHODS AVAILABLE

To determine the absolute intensity of radiation in the vacuum ultraviolet (VUV) from a given source, all but one method requires the calibration of a secondary standard. That calibration is made usually at a wavelength far removed from the VUV. Then, the assumption is made that the detector has a "flat" response to all wavelengths; that is, its quantum efficiency is constant. These secondary standards are usually thermocouples, thermopiles, bolometers, or similar instruments.

The one direct means to determine absolute intensities is based on the photoionization of the rare gases; however, this limits its direct usefulness to radiation below  $1022 \text{ \AA}$  (the ionization potential of xenon). This method is based on the assumption that the photoionization yield,  $\gamma$ , of the rare gases is unity; i.e.,

$$\begin{aligned}\gamma &= \text{ions produced/photons absorbed} \\ &= 1 \text{ (for the rare gases).}\end{aligned}$$

However, if the assumption is accepted, the method resolves itself to the determination of an electric current (ions/sec), which is then related to the absolute number of photons/sec absorbed by the gas. Theoretically,  $\gamma$  is expected to be unity, even in the regions of autoionization which generally occur between the  $^2P_{3/2}$  and  $^2P_{1/2}$  states. The lifetime of these radiationless transitions into the ionization continuum is of the order of  $10^{-15}$  secs and therefore they have an extremely high probability of producing an ion/photon absorbed in the autoionization region.

An experimental approach to the measurement of  $\gamma$  for the rare gases is to measure their yields relative to one gas, say xenon. If these yields all turn out to be constant with respect to xenon, especially in regions of autoionization, then this is excellent evidence that the constant  $\gamma$  must be unity. A further check with a calibrated thermopile may lend confidence to this assumption.

Two ion chambers were designed and constructed to measure the photoionization yields of gases. Figure 1 shows a drawing of a double ion chamber while Figure 2 illustrates a single ion chamber. As far as can be ascertained, the first use of a double ion chamber to measure photoionization yields was by Wainfan, Walker and Weissler.<sup>(2)</sup>

With the aid of Figure 1, an analysis of the double ion chamber is given. Denote  $I_0$  as the incident light intensity to be measured; then, with a gas in the cell at some suitable pressure, denote  $I_1$  and  $I'_1$  as the intensities entering and leaving Plate 1, and denote  $I_2$  and  $I'_2$  as the intensities entering and leaving Plate 2. The three small plates alternating with the ion collection plates are guard rings to provide a uniform field between the parallel plates and are all at ground potential. The repeller plate is held a few volts positive to drive the ions to Plates 1 and 2.

The photoionization yield of a gas is defined as

$$\gamma = \frac{\text{ions produced/sec}}{\text{photons absorbed/sec}}$$



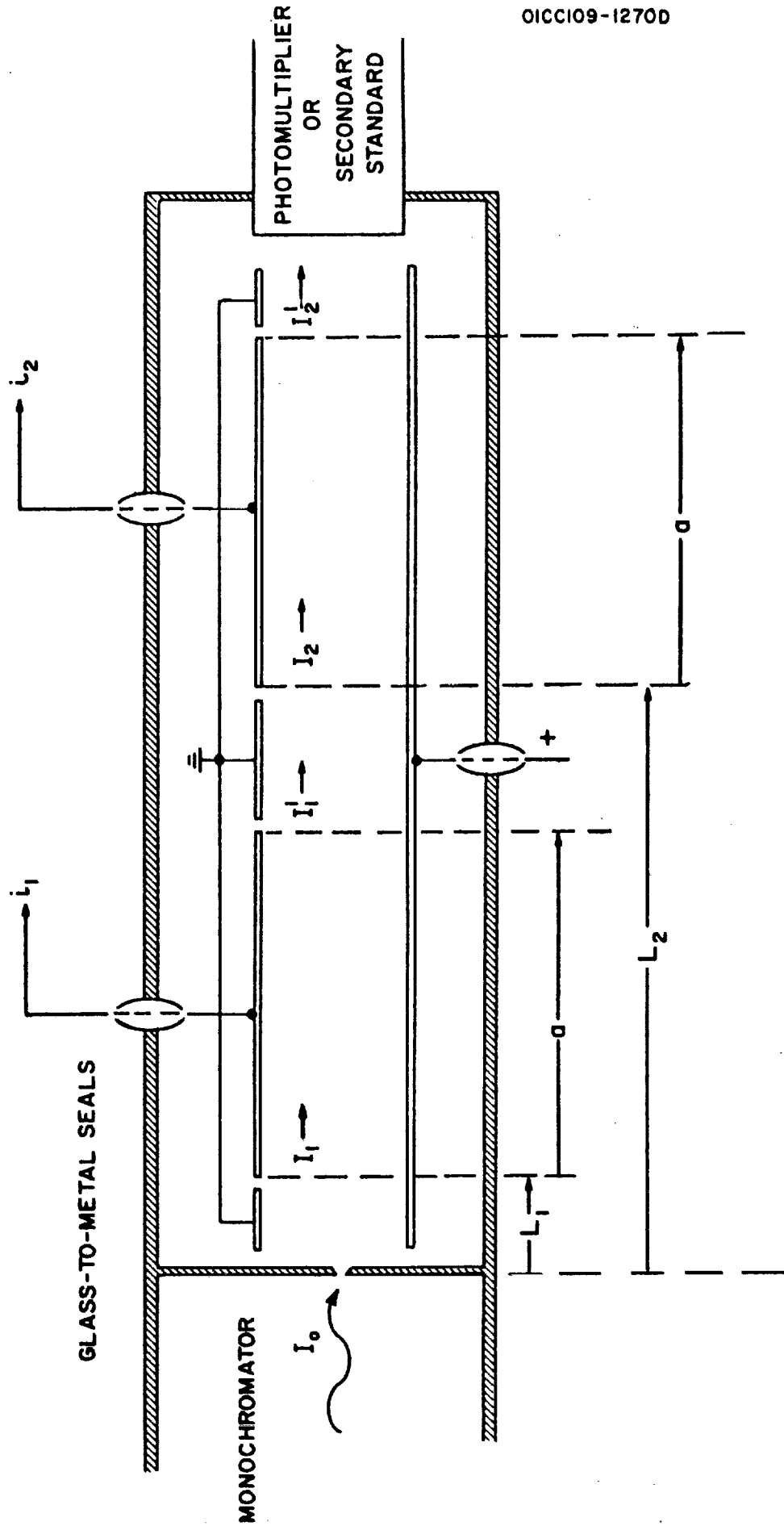


Figure 1. The double ion chamber.  $I_0$  is the flux passing through the exit slit of the monochromator.  $I_1$  and  $I_2$  are the fluxes entering, and  $I_1'$  and  $I_2'$  are the fluxes leaving the ion collector regions of Plate 1 and Plate 2, respectively.

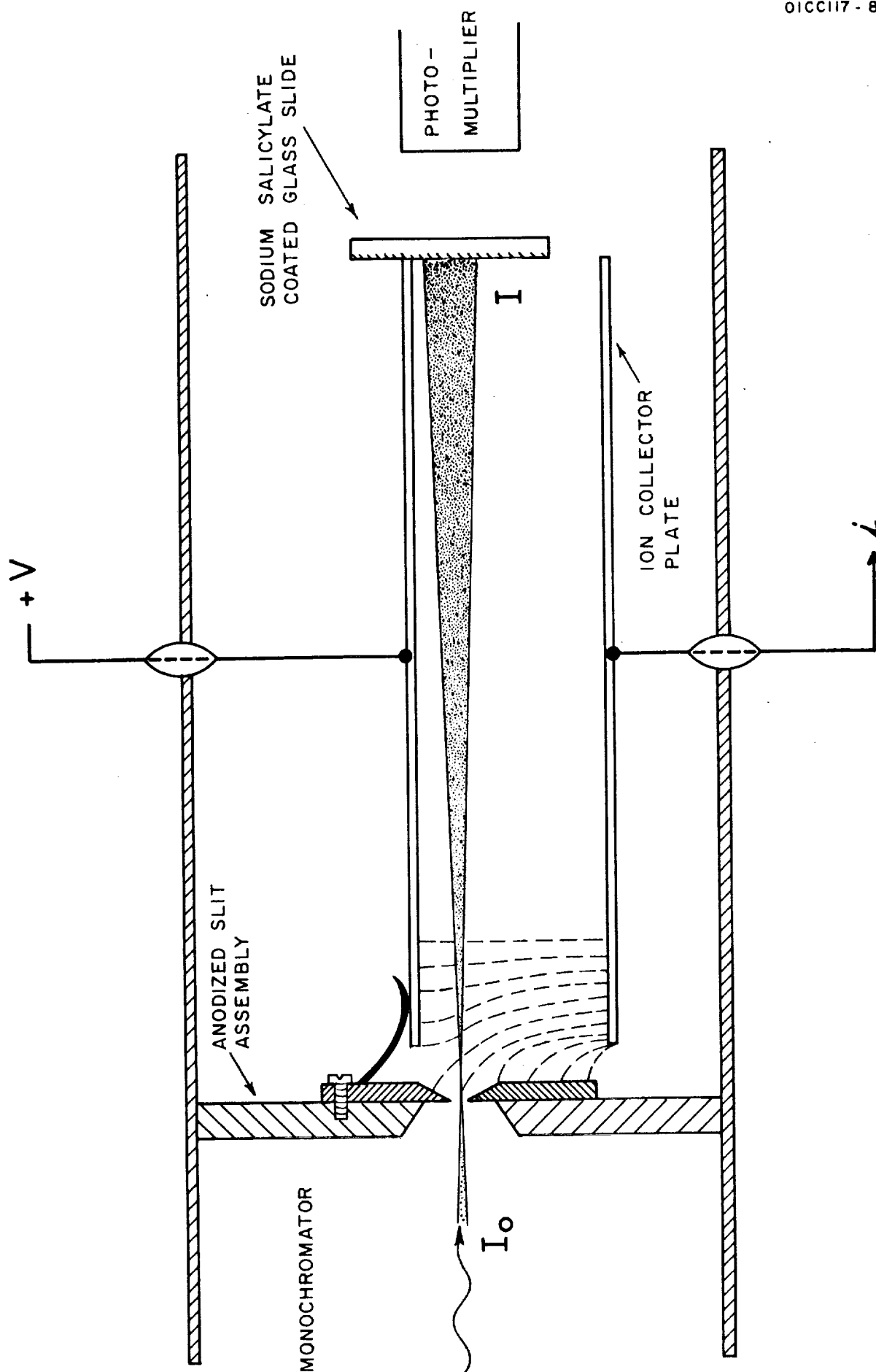


Figure 2. The single ion chamber.  $I_0$  is the flux passing through the exit slit of the monochromator while  $I$  is the flux at the detector. The dashed lines indicate typical electric field lines.

Now at Plate 1, ions produced/sec =  $i_1 / e$

where  $i_1$  is the electric current flow and  $e$  is the electronic charge;  
and further,

$$\begin{aligned}\text{photons absorbed/sec} &= I_1 - I_1' , \text{ using Lambert's Law this becomes} \\ &= I_0 \exp (-\mu L_1) [1 - \exp (-\mu a)]\end{aligned}$$

where  $\mu$  is the absorption cross section of the gas at that pressure and  
 $L_1$  and  $a$  are the dimensions shown in Figure 1:

$$\text{Therefore, } \gamma = \frac{i_1/e}{I_0 \exp (-\mu L_1) [1 - \exp (-\mu a)]}$$

$$\therefore I_0 = \frac{1}{\gamma} \frac{i_1/e}{\exp (-\mu L_1) [1 - \exp (-\mu a)]} \quad (1)$$

Similarly,

$$I_0 = \frac{1}{\gamma} \frac{i_2/e}{\exp (-\mu L_2) [1 - \exp (-\mu a)]} \quad (2)$$

From the ratio (1):(2)

$$\frac{i_1}{i_2} = \exp [\mu (L_2 - L_1)] \quad ;$$

i.e.,

$$\mu = \ln (i_1/i_2) / (L_2 - L_1) \quad .$$

Substituting  $\mu$  into (1) and assuming  $\gamma = 1$ ,  $I_0$  can be found from measurements of  $L_1$ ,  $L_2$ ,  $a$  and the ion currents  $i_1$  and  $i_2$ .

The same procedure is used to measure  $\gamma$  in other gases. When  $I_0$  is known, Eq. (1) is again used and the value of the photoionization yield determined. It should be noted that the absolute value of the gas pressure is not required in those measurements.

Implicit in the double ion chamber method is the use of a measured absorption cross section, and thus the accuracy of the method depends upon the measured absorption cross sections obeying Beer's law which states that "the amount of light absorbed is proportional to the number of absorbing molecules through which the light passes." Incorporated into Lambert's law, this gives

$$I = I_0 \exp (-kx)$$

where  $k$  is the absorption coefficient at S.T.P., while  $x$  is the path length reduced to S.T.P. and is given by

$$x = L \frac{P}{760} \frac{273}{T} .$$

Thus, to obey Beer's law,  $k$  must be independent of both pressure ( $P$ ) and path length ( $L$ ).

The major advantage of the double ion chamber lies in the fact that all the variables—i.e., the two ion currents and the detector output—can be measured simultaneously, thereby eliminating any discrepancies due to light source fluctuations.

Referring to Figure 2 for an analysis of the single ion chamber, we define  $I_0$  as the light intensity at the exit slit of the monochromator and  $I$  as the transmitted intensity at the end of the ion chamber. Then,

$$\begin{aligned}
 \gamma &= \frac{\text{ions formed/sec}}{\text{photons absorbed/sec}} \\
 &= \frac{i/e}{I_0 - I} \\
 &= \frac{i/e}{I_0(1 - I/I_0)} \\
 \therefore I_0 &= \frac{1}{\gamma} \frac{i/e}{(1 - I/I_0)} \quad (3)
 \end{aligned}$$

The ratio  $I/I_0$  is measured by the detector which must lie exactly at the end of the ion chamber. This ratio is independent of absolute intensities and any detector which has a linear response with respect to intensity may be used. This method requires that all the ions formed from the exit slit to the detector be collected and counted. To achieve this, it is necessary to connect the exit slit electrically to the positive repeller plate. The ion chamber would then have a field distribution as shown in Figure 2 and all ions formed within the ion chamber system would be collected. The major advantage of this system is that no measurement of an absorption coefficient is made which must obey Beer's law. Actually,  $I_0$  is independent of the pressure used and in the limit when  $I/I_0 \rightarrow 0$

$$I_0 = \frac{1}{\gamma} i/e \quad (4)$$

### III. EXPERIMENTAL DIFFICULTIES

There is no independent way to check the flatness of a thermopile response to VUV radiation other than a cross check against the rare gas calibration method; however, the following can be said. The metallic "blacks" with which the receivers of a thermopile are coated are actually pure metallic droplets which have been evaporated onto the receivers under appropriate conditions to form spherical droplets of suitable radii to provide minimum reflection of visible and infrared radiation. The receivers thus appear black and essentially absorb all of the incident radiation. For VUV radiation, the wavelengths are reduced by about an order of magnitude or more; thus, the spherical drops will appear larger to this type of radiation and presumably the blackness does not necessarily hold in this region of the spectrum. However, due to the fact that most materials have poor reflectances in the VUV, this may offset the fact that the metallic spheres have a larger ratio of radii/wavelength and the receivers may thus be truly black to VUV radiation. A further point is that all metals show a photoelectric yield in the vicinity of 5 to 10 percent at wavelengths below 1000 Å. This certainly means a loss of photons for the production of heat and thus an error in the determination of the absolute energies.

The use of photoionization techniques for absolute intensity measurements is far from being straightforward. To begin with, since there are no windows available in this spectral region, one must take

care that the main vacuum system of the monochromator is maintained at a high vacuum to insure that the photon intensity at the exit slit of the monochromator is the same before and after the calibrating gas is allowed to flow into the ion chamber.

Probably one of the most important precautions to take is to be certain one is using the proper collector voltage on the ion plates. That is, one must operate in the plateau region of the ions vs. voltage curve; in fact, one must ascertain that there actually is a plateau for the particular ion chamber, calibrating gas, and wavelength used. For example, if xenon were ionized by  $461.5 \text{ \AA}$  (26.86 ev), an electron could be ejected with an energy,  $E$ , given by:

$$E = h\nu - I(\text{Xe}) \quad (5)$$

where  $I(\text{Xe})$  is the ionization potential of xenon and is equal to 12.13 ev.  $h\nu$  is the energy of the incident photon which, in this example, is 26.86 ev.

Therefore,

$$E = 14.73 \text{ ev.}$$

Thus, the electron is emitted with sufficient energy to cause secondary ionization. With the addition of a collector voltage, this energy is increased. It is, therefore, impossible to achieve a plateau with xenon at  $461.5 \text{ \AA}$  and at a pressure which would give a measurable ion current. Figure 3 illustrates this point for a particular ion chamber.

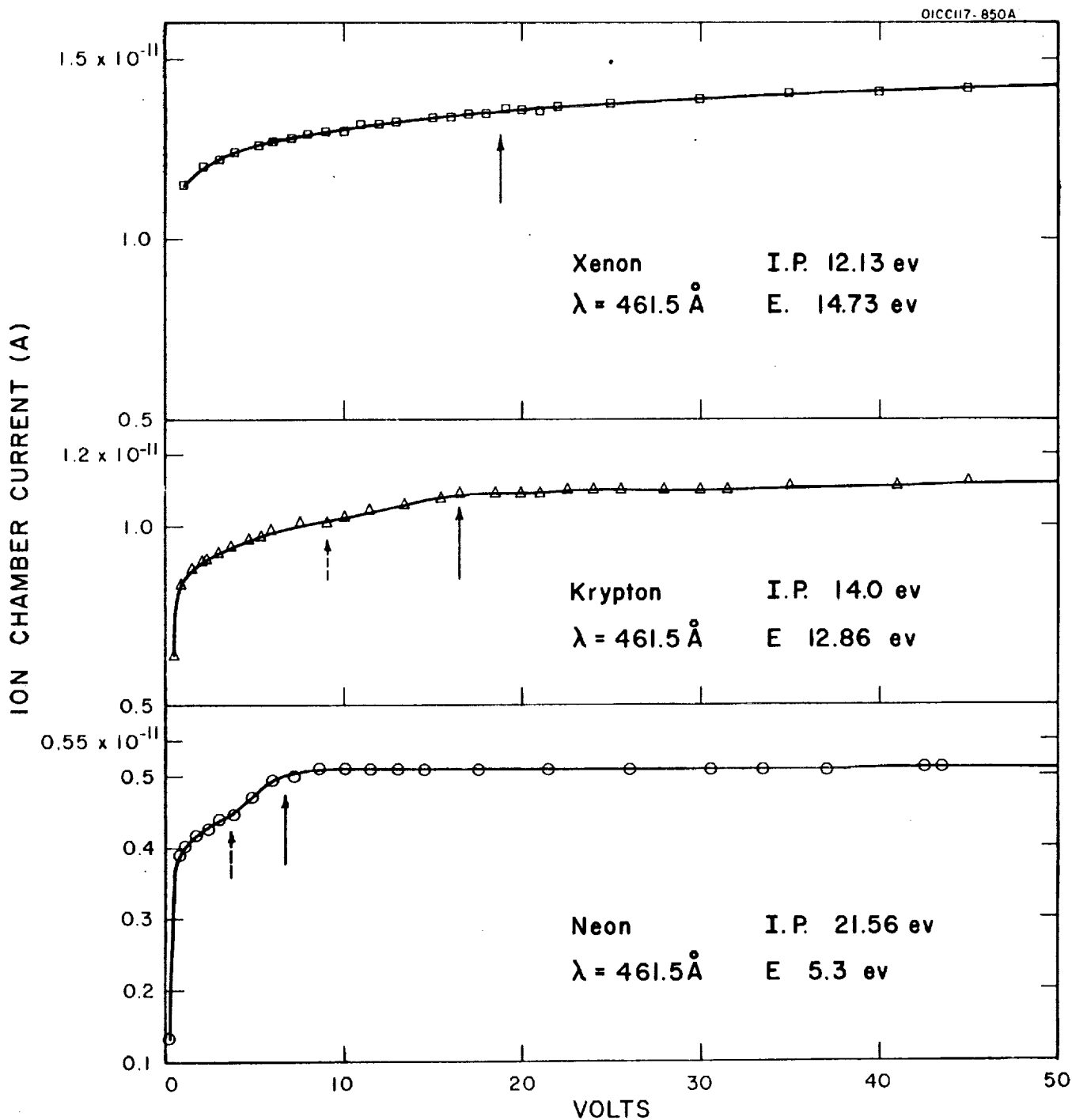


Figure 3.

Ion Chamber Currents as a Function of Voltages for Xenon, Krypton and Neon at  $461.5 \text{ \AA}$ . In each case, the solid vertical arrow indicates the voltage necessary to commence electron retardation whereas the dashed arrow indicates the voltage necessary to complete electron retardation.



A further competing process is the collection of electrons as well as the ions. This can occur if a sufficiently high electron retarding potential is not used. Reference to Figure 4 illustrates possible electron trajectories. Now these electrons all have the same energies, but those travelling at an angle to the field lines can be retarded at lower voltages than those travelling parallel to, but opposing, the field lines. That is, the important quantity is the component of the electron energy normal to the collector plate. It has been shown by Sommerfeld<sup>(3)</sup> that the probability for an electron to be ejected at an angle  $\theta$  to the direction of propagation of the incident radiation is proportional to  $\sin^2\theta$ ; thus, the most probable direction is at right angles to the path of the incident radiation. For a given geometry, this will result in an energy spread between some minimum and maximum energy. The maximum energy, of course, is simply  $E$  as given by Equation (5). Therefore, a curve of ion current versus voltage should indicate a plateau at voltages lower than that necessary to retard the electrons of minimum energy. In this region, all the ions and a fraction of the electrons are collected. At a voltage high enough to retard the electrons of minimum energy, the ion current should start to increase and continue increasing until the voltage is sufficiently high to retard all electrons at which point the true plateau should start. The bottom two curves in Figure 3 show typical curves for krypton and neon, illustrating this point. The arrows indicate the values of the calculated ion chamber voltages to provide the necessary minimum and maximum voltages to retard the electrons.

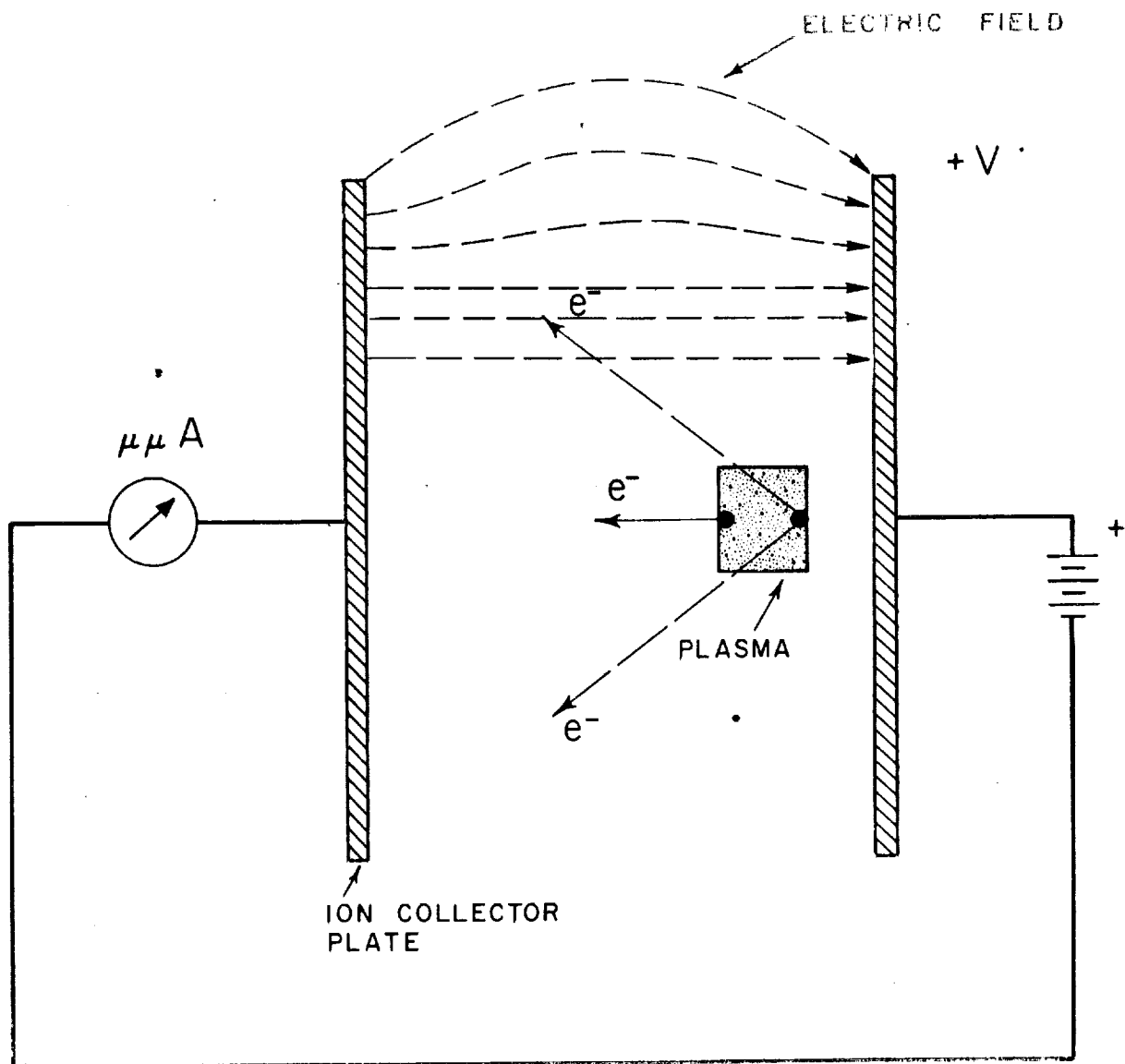


Figure 4. Typical electron trajectories for which the electrons will strike the ion collector plate if a sufficiently high retarding potential is not used.

It is interesting to note that a parallel plate ion chamber can actually analyze the energies of photoelectrons — a very important parameter in determining the state of excitation a molecule is left in after it has been photoionized. These preliminary experiments indicate the feasibility of analyzing the photoelectron energies with higher precision using a more sophisticated system.

#### IV. RESULTS

Preliminary intensity measurements of VUV radiation have been made by the technique of photoionizing rare gases and assuming that their photoionization yield,  $\gamma$ , is unity. We have set out to show that this assumption is indeed a good one. Data have also been obtained on the quantum efficiency of sodium salicylate in the previously unexplored region between 400 Å and 900 Å, and on the photoelectric yield of aluminum. Finally, thermopile measurements have been initiated.

In the photoionization of the rare gases using a single ion chamber the experimentally determined quantity, as given by Equation (3), is the product of the absolute radiation intensity with the photoionization yield; that is,  $I_0\gamma$ . Now, if the light source intensity is kept constant — and hence  $I_0$  — and the quantity  $I_0\gamma$  measured for each of the rare gases which will ionize in that region, then the ratio of these values will give the relative photoionization yields  $\gamma_1/\gamma_2$  of the rare gases. Should the rare gases all have identical yields, this ratio will be unity. Figure 5 shows a plot of the relative yields of argon, xenon, krypton, and neon, with respect to wavelength. The ratio of the yields is unity with an error spread of  $\pm 5\%$ . It is extremely unlikely that the photoionization yield curves can show structure which is identical for all the rare gases. Thus, the most probable value for the photoionization yield of the rare gases is unity even in the regions of autoionization. This result agrees with what one expects theoretically.

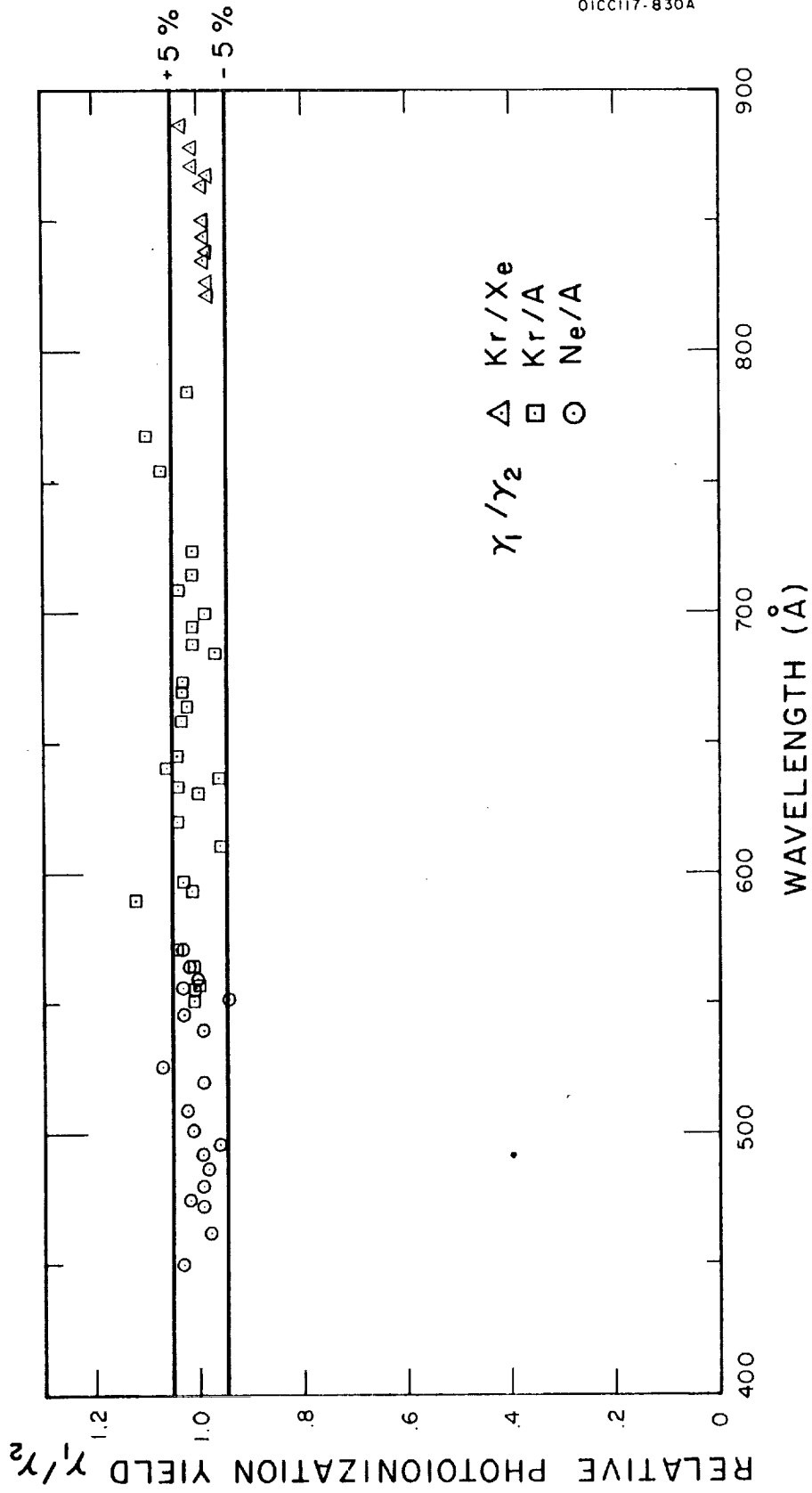


Figure 5. The relative photoionization yield of the rare gases in the region 400 - 900 Å. Kr/Xe represents the yield of krypton relative to Xenon, etc.

The thermopile data were taken with 0.5 mm x 3 mm slits on a half meter Seya monochromator. This gave a  $\lambda$  pass band of 16 Å. Lyman-alpha gave a response of 0.18  $\mu$  volts. The receiver elements of the compensated thermopile had a poor coating of gold black which might render it less sensitive to the longer wavelengths, since these will be preferentially reflected.

The thermopile was uncalibrated, but was used as a detector with a flat response as a function of wavelength. Since the thermopile is an energy measuring device, its output (V) in  $\mu$  volts was multiplied by  $\lambda$ ; this converted the data to a quantity proportional to photons/sec. Thus, the yield of sodium salicylate is defined in relative unity as the output of the coated photomultiplier (i) divided by  $V\lambda$ ; i.e.,

$$Y = \frac{i}{V\lambda} .$$

The thermopile vacuum-to-air sensitivity was measured and found to be six times.

Figures 6 and 7 give the relative quantum yield of sodium salicylate as a function of wavelength in the range 400 to 1600 Å. The yield was determined between 400 to 1020 Å using the rare gas technique to calibrate the light intensity. The quantum yield in this case is actually defined as the output current of a sodium salicylate-coated photomultiplier divided by  $I_0\gamma$ . A Reeder type thermopile was used in the range 900 to 1600 Å (Figure 7). Included in this Figure are the results using

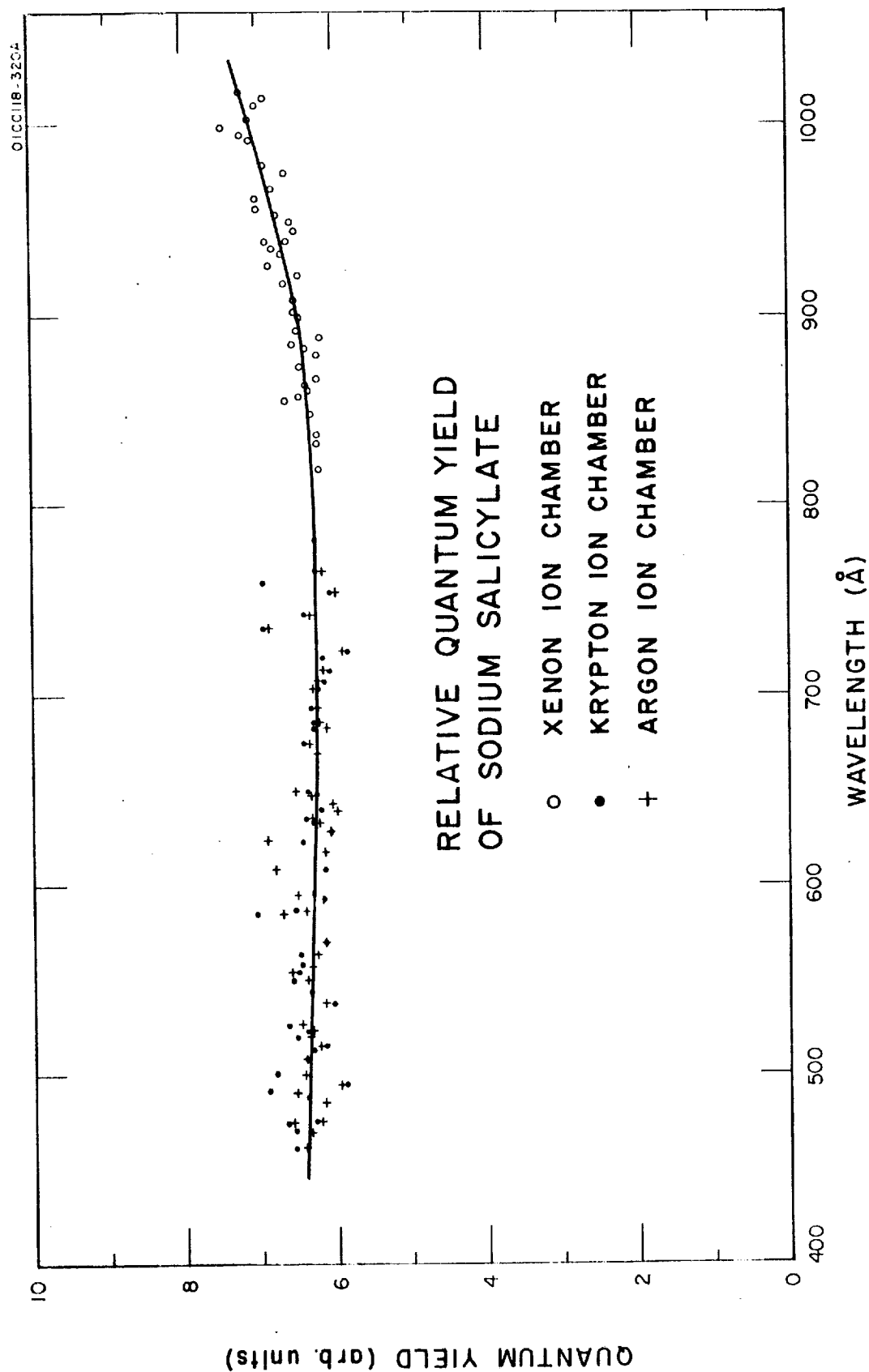


Figure 6. Relative quantum yield of sodium salicylate as a function of wavelength in the range 400 - 1000Å. The intensity of the incident radiation was measured by an ion chamber filled with a rare gas.

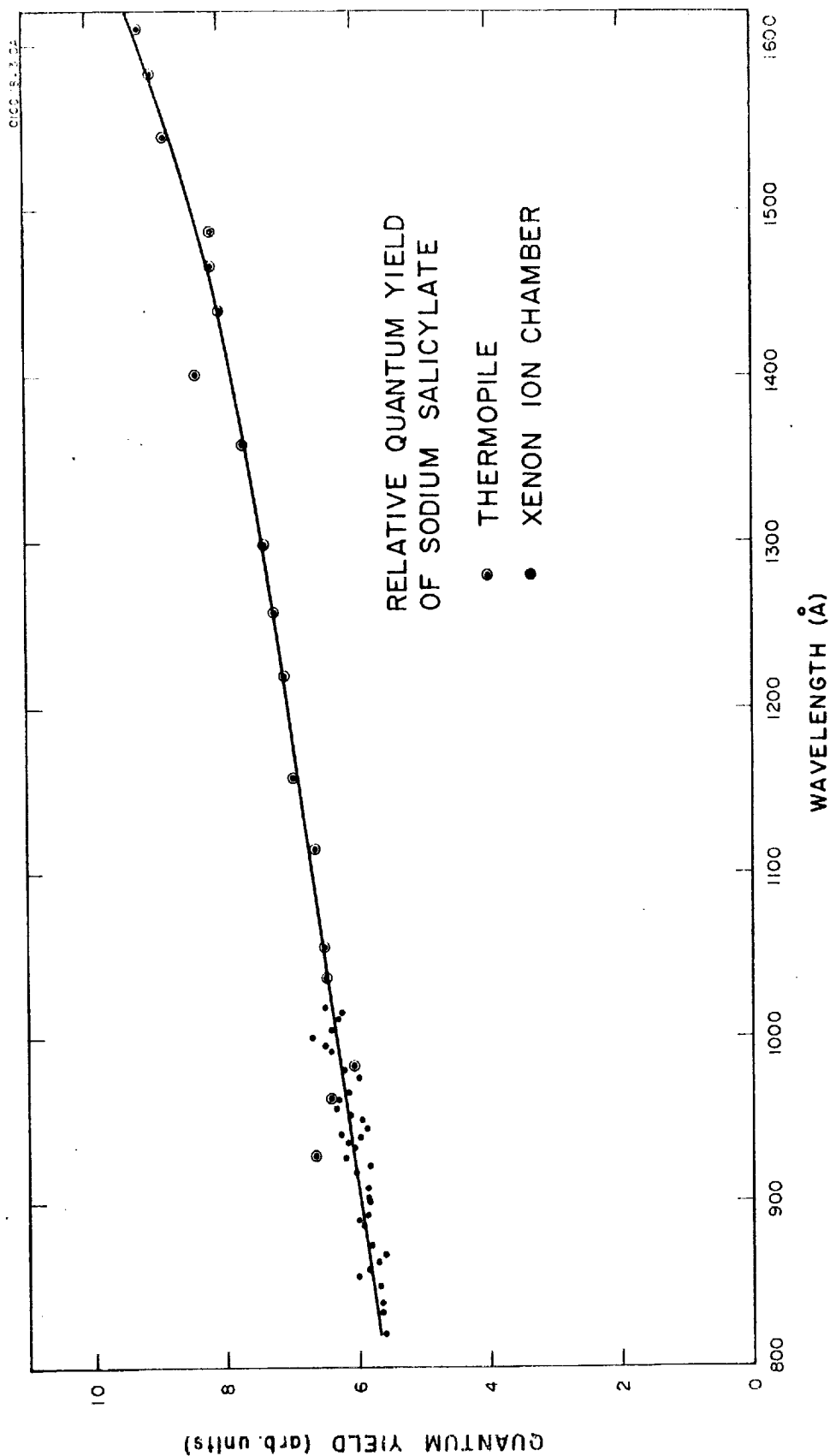


Figure 7. Relative quantum yield of sodium salicylate as a function of wavelength in the range 800 - 1600Å. The solid data points represents data taken with a xenon ion chamber while the other points were taken with a thermopile which was assumed to have a "flat" response.



a xenon ion chamber. The actual curve was normalized to fit onto the thermocouple curve since the data were taken on different days. We noticed a continual decrease in the yield of sodium salicylate from day to day. Typically, a decrease of 25 percent was found for a one-day old coating.

The data above 900 Å appear to be in conflict with that reported by Johnson et al.<sup>(4)</sup> and by Watanabe;<sup>(5)</sup> however, the fact that both the xenon ion chamber and the thermopile data show the same increase towards longer wavelength lends strong support that this increase is real. However, further work is in progress to reproduce this curve with another thermopile with a very black receiver. The curve shown here must be considered as a preliminary result; however, it does point up the problem in assuming that all salicylate coatings have a constant quantum yield below 1600 Å.

The photoelectric yield of aluminum, with 4% magnesium, was measured and found to have a yield in excess of 10% in the range 450 to 1000 Å. It had a peak efficiency of 18% at 760 Å. Figure 8 gives the yield as a function of wavelength.

The aluminum was cut from standard stock material, type 5086-H32, and was highly polished. Before measuring the yield, it was cleaned with acetone. The yield reported here is higher than that of any metal yet reported in the vacuum ultraviolet.<sup>(6)</sup>

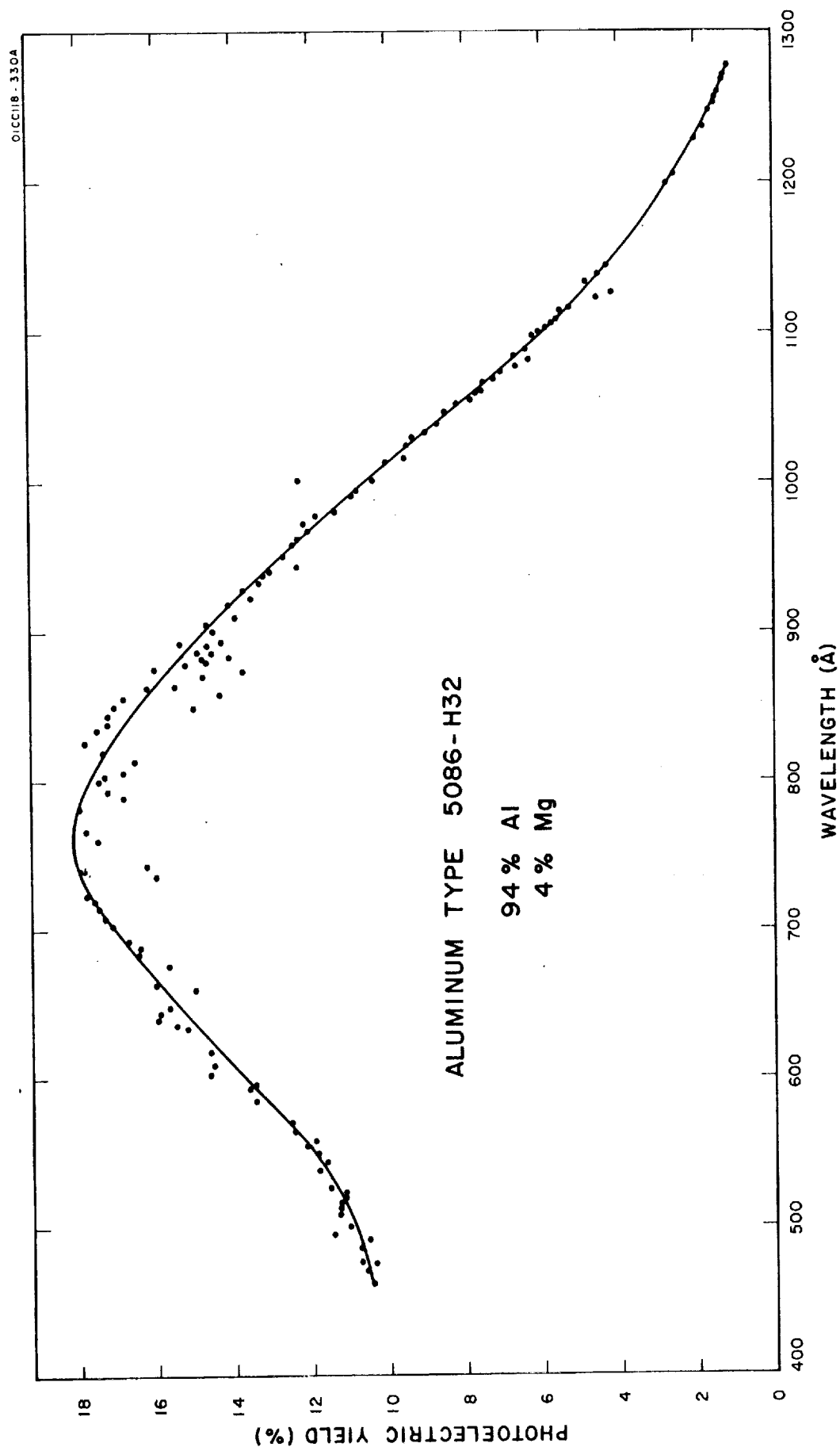


Figure 8. Photoelectric Yield of Aluminum as a Function of Wavelength. The absolute yields were determined using the rare gas ionization chambers.

## V. CONCLUSIONS

The relative photoionization yields of the rare gases with respect to one another is unity. Thus, absolute intensity measurements will be independent of which rare gas is used, provided proper experimental care is observed; for example, measurements must be made on the plateau region of the ions vs. voltage curve, no stray electrons should be collected, and measurements in the vicinity of discrete absorption peaks should be avoided unless the single ion chamber is used.

#### REFERENCES

1. Samson, J.A.R., J. Opt. Soc. Am. 52, 525 (1962).
2. Wainfan, N., Walker, W.C. and Weissler, G.L., J. Appl. Phys. 24, 1318 (1953).
3. Sommerfeld, A., Wave Mechanics (Methuen & Co., Ltd: London, 1930), p. 181.
4. Johnson, F.S., Watanabe, K. and Tousey, R., J. Opt. Soc. Am. 41, 702 (1951).
5. Watanabe, K. and Inn, E.C.Y., J. Opt. Soc. Am. 43, 32 (1953).
6. Walker, W.C., Wainfan, N. and Weissler, G.L., J. Appl. Phys. 26, 1366 (1955).